



Photochemical modelling in the Po basin with focus on formaldehyde and ozone

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**Modelling of
formaldehyde and
ozone**

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Photochemical modelling in the Po basin with focus on formaldehyde and ozone

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As part of the EU project FORMAT (Formaldehyde as a Tracer of Oxidation in the Troposphere), a field campaign was carried out in the vicinity of Milan during the summer of 2002. Results from a 3-D regional chemical transport model (NILU RCTM) were used to interpret the observations focusing primarily on HCHO and ozone. The performance of the model was assessed by comparing model results with ground based and aircraft measurements. The model results show good agreement with surface measurements, and the model is able to reproduce the photochemical episodes during fair weather days. The comparison indicates that the model can represent well the HCHO concentrations as well as their temporal and spatial variability. The relationship between HCHO and ($O_3 \times H_2O$) was used to validate the model ability to predict the HCHO concentrations. Further analysis revealed the importance of the representativity of different instruments: in-situ concentrations might be locally enhanced by emissions, while long path measurements over a forest can be influenced by rapid formation of HCHO from isoprene. The model is able to capture the plume from the city of Milan and the modelled levels agree generally well with the aircraft measurements, although the wind fields used in the model can lead to a displacement of the ozone plume. During the campaign period, O_3 levels were seldom higher than 80 ppbv, the peak surface ozone maxima reached 90 ppbv. Those relatively low values can be explained by low emissions during the August vacation and unstable weather conditions in this period. The modelled $\Delta O_3 / \Delta NO_z$ slope at Alzate of 5.1 agrees well with the measured slope of 4.9.

1 Introduction

Ozone (O_3) is harmful both to humans and vegetation, and the extent of damage depends on the concentration of ozone and the duration of exposure (Heck et al., 1982; Gong et al., 1986). The surface ozone levels at European rural and remote sites have

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increased by more than a factor of two from the beginning of the industrialization (Volz and Kley, 1988; Anfossi et al., 1991; Marenco et al., 1994; Staehelin et al., 1994; Pavelin et al., 1999) because of the large increase in the emissions of ozone precursors during this period. Ozone builds up to toxic levels in the atmosphere during warm, sunny weather when pollutants mainly nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), CO and volatile organic carbons (VOCs) accumulate in stagnant air. Ozone levels in polluted areas can be elevated to more than 100 ppbv in a few days under favourable weather conditions (e.g. Isaksen et al., 1978; Prévôt et al., 1997). Many regulations have been applied to reduce ozone levels in the last decades, but the improvements are limited, especially for the rural areas (Solberg et al., 2004, 2005; Ordóñez et al., 2005). This is because the ozone production is highly non-linear and controlled by VOC, CO and NO_x . The ozone production per unit NO_x depends on the VOC/ NO_x ratio, VOC reactivity and the NO_x levels (Isaksen et al., 1978; Liu et al., 1987; Lin et al., 1988). Besides the influence of anthropogenic emissions of ozone precursors, highly reactive biogenic emissions, especially of isoprene, add uncertainties to the ozone production and distribution both in urban and rural areas (Trainer et al., 1987; Chameides et al., 1988).

Formaldehyde is the most abundant carbonyl compound in the atmosphere. It can be directly emitted from incomplete combustion processes, or produced by photooxidation of hydrocarbons. The direct emissions mostly come from biomass burning or combustion engines. Precursor hydrocarbons, which give rise to secondary formaldehyde, also have many different anthropogenic and biogenic sources. The formaldehyde concentration level varies from several tens of pptv in clean background air, to tens of ppbv in hydrocarbon rich air. As an intermediate in the oxidation of hydrocarbons to carbon monoxide (CO), HCHO plays an important role in the hydrocarbon oxidation chain and CO budget. Through photolysis and reaction with the hydroxyl radical (OH), HCHO acts as an important source for the hydroperoxyl radical (HO_2), which leads to ozone production when NO_x is present. Because of its widespread presence and its role in photooxidation, HCHO is a key component for local, regional and large-scale

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photochemical processes and budgets.

Accurate measurements of HCHO are therefore important for the understanding of odd hydrogen species (OH and HO₂), ozone production and the global CO budgets. Highly sensitive techniques are required to measure HCHO under different circumstances. HCHO measurements were performed in several projects in the last two decades (e.g. Harris et al., 1989; Heikes et al., 1996; Hov and Flatøy, 1997), and differences between various types of HCHO measurements were found (Gilpin et al., 1997; Cárdenas et al., 2000). These discrepancies were considered to be caused by different techniques, or by the instruments setup. One of the main objectives of the FORMAT project was to gain a better understanding of the disagreement between different measurement techniques. Hence, an intensive comparison between different in-situ measurement methods was performed during the 2002 campaign in the Po Basin. The results indicate that there is a good agreement between different techniques as long as the same air mass is measured, and that the observed disagreements are mainly caused by different instrument setups (Hak et al., 2005).

The Milan metropolitan area has a population of about 4 million and is the most industrialized and populated area in northern Italy. Episodes with high photooxidant levels are frequently observed in this region. In previous campaigns in the Po Basin, such as the POLLUMET campaign in 1992 and the PIPAPO campaign in 1998, O₃ mixing ratios up to 185 ppbv and 190 ppbv were measured, respectively (Prévôt et al., 1997; Neftel et al., 2002; Dommen et al., 2002; Thielmann et al., 2002). These studies focused on the ozone production and VOC/NO_x sensitivity. Both measurements and the model results concluded that the ozone production is VOC limited within the Milan plume, and NO_x limited in the surroundings. The previous studies show that the highest O₃ levels are mostly found in VOC controlled regimes, approximately 30 km downwind of the emission sources (Prévôt et al., 1997; Martilli et al., 2002; Thielmann et al., 2002; Baertsch-Ritter et al., 2003, 2004; Andreani-Aksoyoglu et al., 2004). HCHO is present in high concentrations in this area as well, directly emitted (mainly from vehicles) or produced from oxidation of hydrocarbons. Typical levels about 10 ppbv

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and a peak value up to 33 ppbv were observed in the summer month, downwind of the Milan metropolitan area (Staffelbach et al., 1997; Alicke et al., 2002).

To achieve the goal of improved air quality, better scientific tools for understanding and reproducing the photochemical smog episodes are needed. Many comprehensive numerical models have been developed to simulate the photochemical processes in Europe. In addition to supply scientific support to emission abatement, numerical models can also be used for the forecasting of air pollution events. Tilmes et al. (2002) evaluated five Eulerian state-of-the-art chemical transport models including NILU RCTM, and concluded that the most comprehensive models give the best results. The NILU RCTM has been used in several European Union projects (TACIA, ACSOE, POLINAT, MAXOX, INCA, ACTO), which involved aircraft measurements. The model provided chemical forecasts for the planning of the flight routes (Flatøy et al., 2000). During the FORMAT campaign the model was used for the same purpose. The model results were evaluated with various measurements from surface and aircraft, and show a good ability to reproduce the photochemical evolution present in the measurements. In this paper, based on the intensively measured HCHO dataset, a more detailed model evaluation is presented. With a better understanding of discrepancies between different HCHO measurement techniques, the model performance has been evaluated against the observations. For the first time, this model has been used to interpret the photochemical evolution in a very polluted region with complex terrain.

2 The FORMAT 2002 campaign

2.1 Time period and measurement platforms

The campaign was carried out in the Po Basin, Italy from 22 July to 20 August 2002. The Po Basin was chosen for the FORMAT campaign in order to capture the photochemical transformation of the Milan photooxidation plume, and to achieve a better understanding of the evolution of formaldehyde and its roles in a highly polluted area.

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During the campaign ground-based measurements of HCHO and additional species were carried out at two sites located in the north of Milan city (Fig. 1). The site at Alzate, used as a semi-rural station, is located downwind and about 35 km north of Milan, close to the foothills of the Alps, and 404 m a.s.l. The other site, at Bresso, is an urban station in the northern outskirts of Milan city, also downwind, but influenced by direct emissions from the city. For a detailed description of Alzate and Bresso see Thielmann et al. (2002).

An ultralight aircraft operated by IMK-IFU carried out airborne measurements during the campaign. The aircraft was based at the airfield of Lecco Monte Marengo, a small airport located 10 km south of Lecco and about 35 km northeast of Milan. The typical flight routes covered regions north of Milan and up to 30 km east of Milan. There were also two days where the flights were performed about 50 km to the south of Milan (13 and 15 August). Each aircraft mission lasted around three hours. The flight height followed the airspace regulations: it was about 600 m a.s.l. in the plain and up to 2700 m a.s.l. in the Alpine foothills. The aircraft measurements focused on HCHO, O₃ and aerosols. Meteorological parameters were recorded along the flight routes. Onboard the ultralight aircraft, formaldehyde was measured with a Hantzsch instrument (Kelly and Fortune, 1994). The detection limit for HCHO is ~50 ppt with a delay time of 90 s, and, assuming a flight velocity of 20 m/s, the horizontal resolution is about 2 km. The instruments on the ultralight aircraft are described in detail by Junkermann et al. (2005).

2.2 Instrumentation and species

One of the most important objectives of the FORMAT project was to compare and improve the different measurement techniques used for measuring formaldehyde in the atmosphere. Therefore, HCHO was intensively observed with various existing measurement techniques during the 2002 FORMAT campaign. The DNPH-HPLC method (Lee and Zhou, 1993) has been the main technique for the detection of formaldehyde, but new instruments with better time resolution and improved detection limits are now

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available. Among those, spectroscopic techniques like DOAS (Differential Optical Absorption Spectroscopy) (Cárdenas et al., 2000) and FTIR (Fourier Transform Infrared Spectroscopy) (Lawson et al., 1990), and a fast in-situ Hantzsch technique using liquid phase fluorimetric detection have been widely used.

During the campaign period, five Hantzsch instruments were operated by three institutes for in-situ measurements of HCHO. Both the FTIR technique and the DOAS technique were used with White systems (White, 1976) for quasi in-situ measurements. The instruments and techniques were described by Hak et al. (2005). At the same time, a Long Path DOAS (LP-DOAS) was used for remote sensing at Alzate. With the purpose of understanding the ozone photooxidation processes, additional species, such as O₃, CO, NO, NO₂, NO_y (NO+NO₂+NO₃+N₂O₅+PAN+HNO₃+HONO), HNO₃, and PAN were measured. Table 1 gives a description of the instruments used and species measured during the 2002 campaign. Meteorological stations were operational at both sites.

2.3 Meteorological conditions

The meteorological conditions during the 2002 campaign period were characterized by more unstable weather than usual. Temperatures were lower, and there was more precipitation than usual. During the FORMAT campaign, three fair weather periods were identified. The first period was from 22 to 31 July. This period was dominated by a high-pressure system, and high radiation during daylight hours (average above 350 W/m² between 08:00–20:00 LT). Temperatures exceeded 30°C only on 31 July. After a few unstable days with short shower events, 7–8 August again showed fair weather conditions with high radiation and moderately high temperatures. During the period from 9 to 12 August, a low-pressure system associated with precipitation passed over the area. The last days of the campaign, from 13 to 20 August, were again dominated by a high-pressure system, leading to stable weather, and favourable conditions for photochemical reactions. Six flights were carried out during the last fair weather days, and an intensive observation period (IOP) was held during this period.

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The wind patterns during summer in the Po Basin are strongly controlled by thermodynamic circulation. Due to the presence of the Alpine foothills in the north, the dominating winds are northerly during nighttime, and southerly during the day. As a consequence, ozone peaks are often found in the afternoon downwind of Milan, in the north of the Po Basin. Several studies for this area have shown the wind evolution and observed high ozone levels north of Milan during the summer months (Prévôt et al., 1997; Martilli et al., 2002; Thielmann et al., 2002; Baertsch-Ritter et al., 2003, 2004; Andreani-Aksoyoglu et al., 2004). During the 2002 campaign, the meteorological stations at Alzate and Bresso showed similar wind patterns as in other years. Winds blew from the north during the night and early morning, turned to southerly before noon, and changed to northerly in the evening again. The turning time of the wind direction is important for the transport of the Milan plume.

Three North Foehn days (7, 12 and 13 August) were identified during the campaign period according to the criteria described by Forrer et al. (2000). The North Foehn brings air masses from the free troposphere above the Alpine crest to the boundary layer, and is characterized by strong winds and low relative humidity. Meanwhile, differences in pressure and potential temperature are small between stations in the Po Basin and the high-altitude stations in the Alps. During North Foehn events, the air quality south of the Alps and in the highly polluted Po Basin is clearly improved compared to other days. The frequency of North Foehn days is about 4–6% during the summer months (Weber and Prévôt, 2002). Meteorological data from Jungfraujoch (3600 m a.s.l.) and Alzate (404 m a.s.l.) were used to identify the North Foehn days. Figure 2 shows the time series of pressure, temperature, radiation, relative humidity, wind direction and wind speed at Alzate during this period. The three North Foehn days are marked by dashed lines.

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3 Model description

3.1 Model description

The NILU regional chemical transport model (RCTM) is driven by meteorological data from a Numerical Weather Prediction (NWP) model, which is based on the NORLAM model from the Norwegian Meteorological Institute (Grønås et al., 1987; Nordeng, 1986). Global meteorological analyses and forecasts from ECMWF (European Centre for Medium Range Weather Forecasts) are used as initial and boundary conditions. The model uses sigma coordinates and stereographic map projection. Horizontal resolutions of the model can be defined from 150 to 15 km at 60° N. The model uses one way nesting and provides the coarse scale chemistry output as boundary conditions for the fine scale model. A detailed description of the chemistry transport model can be found in Flatøy and Hov (1996).

In the transport part of the CTM, a second-order version of the advection scheme by Bott (1989) is used, and the semi-Crank-Nicholson scheme is used for diffusion. The vertical transport occurring in convection is calculated with a modified version of the asymmetrical convection model (ACM) proposed by Pluim and Chang (1992). Parameterization of the vertical transport of chemical tracers in connection with convective plumes and the compensating sinking motion was introduced by Flatøy and Hov (1995). Dry deposition rates are computed as a function of latitude, time of day, time of year, land type, vegetation type, and meteorological conditions according to McKeen et al. (1991) and Hass (1991). The wet deposition is calculated based on the rate of precipitation at the ground, on the rainout rate from the individual vertical layers, and on the wet scavenging coefficients for individual species. For more details about dry and wet deposition see Hov et al. (1988), Strand and Hov (1994) and Flatøy and Hov (1995).

The chemistry scheme in the NILU RCTM includes a comprehensive description of gas phase chemistry with particular emphasis on photochemical oxidants. The chemistry scheme is documented by Flatøy and Hov (1995, 1996). The chemistry is rather

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similar to the one used in the global two-dimensional model by Strand and Hov (1994) to study global tropospheric ozone. A lumped chemistry scheme is used in the model. The chemical description includes about 110 reactions involving 55 species in the gas phase, aerosol loss is parameterized.

5 Surface emissions are specified for NO_x , CO, VOC and SO_2 . In this study, the emissions from CITY_DELTA (<http://aqm.jrc.it/citydelta/>) for the Milan region were employed for the 15 km grid, emissions from EMEP for 2002 (Berge, 1997) were used on the 50 km grid and on the 150 km domain data from EDGAR (Van Aardenne et al., 2001) for 1995 were used. Emissions were employed with monthly/weekly/hourly variation
10 factors. Natural VOC emissions, as a major source of biogenically produced HCHO, were represented by isoprene in the model. The model calculates the isoprene emission from data on forest cover (land use and forest type) and surface temperature, using a method from Lübker and Schöpp (1989).

3.2 Model set up

15 In this study, the nested model was defined with the horizontal resolutions of 150, 50 and 15 km, 10, 18 and 30 unequally spaced vertical levels were used, respectively, with a model top defined at 100 hPa. Figure 1 shows the model domains with resolution of 50 km and 15 km. Meteorological analysis from ECWMF are used as initial and boundary conditions for NWP prognoses on the three domains, and the meteorological
20 forecasts are stored with one-hour resolution. The 150 km resolution grid covers most of the Northern Hemisphere, and initial and boundary values for all components are fixed to values that are representative for an unpolluted atmosphere. The 50 and 15 km models receive boundary input from the 150 and 50 km grids, respectively. Model results were stored with 3-h resolution for comparison with surface measurements during
25 the whole campaign period. For the days with aircraft observations, model results were stored with one-hour resolution.

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4 Results and discussion

4.1 Comparison of model results and measurements of HCHO

4.1.1 Bresso

From 23 to 31 July, the ground-based in-situ instruments for HCHO measurements were operated at Bresso for intercomparison. In order to compare with the in-situ instruments, both DOAS and FTIR measurements were carried out with White systems. Five Hantzsch instruments run by three participants analyzed the air from a common inlet line. Figure 3a gives a diagram of the instrument setup at Bresso. The use of the White systems for the optical techniques excluded spatial gradients of HCHO as potential error sources, and ensured the sampling of nearly the same air masses by all instruments. The instrument intercomparison experiment concluded that the agreement between different techniques or similar techniques for HCHO measurements of the same air mass was good. The detailed discussion about equipment setup and data analysis was described and discussed by Hak et al. (2005).

The model results for HCHO at Bresso show fairly good agreement with the measurements, but there are some peaks in the measurements that are not captured by the model (second panel of Fig. 4). However the bulk part of the modelled and measured concentrations are in the same range of 2–6 ppbv. This site is exposed to emissions from the city when the winds are from the south, and emissions from the industrial area in the northern part of Milan, when the wind blows from the north. Some HCHO peaks that are not reproduced by the model are possibly caused by primary emissions in the immediate vicinity of the measurement site.

4.1.2 Alzate

In this section, we will focus on the results from Alzate, where both remote sensing (long path DOAS) and in-situ (Hantzsch) instruments were deployed. Figure 3b gives

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a scheme of the instrument setup at Alzate. The site is close to a small airfield, on the edge of a maize field. The Hantzsch instrument was inside a container, with an inlet about 2.5 m above the ground. The LP-DOAS telescope was inside another container, and the retro-reflector array to reflect the light beam was 2190 m away and 35 m above the ground on a telecommunication tower. The light path of the LP-DOAS crossed the maize field and grassland in the first 200 m, and beyond them there was dense forest underneath. Because of the vegetation and anthropogenic activities, high concentrations and variability might be possible at Alzate as well. The HCHO measurements from both instruments agree well during days when the radiation was low. On days with high radiation, there were significant differences between HCHO measurements by the Hantzsch instrument and long path DOAS as it will be discussed in the next paragraph. On some days the LP-DOAS measured twice as much HCHO as the Hantzsch instrument.

The model results agree well with the Hantzsch measurements, and do not show very large variations during the day as LP-DOAS measurements sometimes do (see Fig. 4). The median values between 12:00 h and 17:00 h of the three datasets were calculated for fair weather periods: 1.95 ppbv for Hantzsch, 3.60 ppbv for LP-DOAS, and 2.06 ppbv for model results, respectively. The median levels between 08:00 h and 11:00 h during the same period were 1.22 ppbv for Hantzsch, 2.03 ppbv for LP-DOAS, and 1.57 ppbv for model results. The high levels of HCHO observed by the LP-DOAS are most probably caused by biogenic emissions, because the light path of the LP-DOAS mostly passes over a forest where HCHO is formed from isoprene emitted underneath. Isoprene is a reactive hydrocarbon that is released mainly by deciduous forests, particularly on days with high temperature and radiation. The isoprene levels reach about 1 ppbv between 12:00 h and 17:00 h in Alzate, and evening peaks up to 3 ppbv were measured during the IOP (Steinbacher et al., 2005b). Those measurements were made close to the container, about 200 m away from the forest, so the isoprene levels above the forest in the afternoon hours could be much higher. The isoprene emissions estimated by Steinbacher et al. (2005b) show that the highest levels

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are expected during the afternoon hours. The modelled HCHO concentrations are between the Hantzsch and LP-DOAS measurements and this is expected, since the area of the isoprene-emitting forest is averaged over the whole grid cell. This explains why the model provides less formaldehyde than the LP-DOAS, whose light beam passed directly over a forest area, and also why the model calculates more HCHO than the in-situ measurements, which are hardly influenced by isoprene emitting trees. This result shows that the instrument setup is crucial in order to obtain HCHO measurements that are representative for a larger area, such as a model grid cell of $15 \times 15 \text{ km}^2$. This argument will also apply to other short-lived species that are emitted by or rapidly formed from local sources.

The main source of secondary HCHO is the oxidation of VOCs by reaction with the OH radical. As a consequence, the production of HCHO can be considered proportional to the VOCs and the OH radical content of the air (R1). The photolysis of ozone to form excited atomic oxygen $\text{O}(^1\text{D})$ and the subsequent reaction between $\text{O}(^1\text{D})$ and water are usually the major source of OH in the afternoon for clean air. Therefore, production of [OH] can be approximated by reaction (R2). Considering the loss of HCHO, photolysis of HCHO is a major loss process during the day with clear sky. Both $J(\text{HCHO})$ and $J(\text{O}(^1\text{D}))$ are proportional to the incoming actinic flux. Since radiation contributes both to HCHO production and loss, we might disregard the photolysis terms and investigate the relationship between HCHO and $(R_{\text{VOC}} \times \text{O}_3 \times \text{H}_2\text{O})$ by combining the Reactions (R1) and (R2). If two different instruments, such as Hantzsch and LP-DOAS, give different HCHO amounts for the same value of $(\text{O}_3 \times \text{H}_2\text{O})$, this most probably means that the different air masses probed by the two measurements must contain different amounts of reactivity weighted VOCs. We will in the following use scatter plots of HCHO vs. $(\text{O}_3 \times \text{H}_2\text{O})$ to further compare model results and measurements.

$$P(\text{HCHO}) \propto \sum_{i=1}^N k_i \times [\text{VOC}_i] \times [\text{OH}] \equiv R_{\text{VOC}} \times [\text{OH}] \quad (\text{R1})$$

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Where R_{VOC} is reactivity weighted VOC

$$P(\text{OH}) \cong [\text{O}_3] \times [\text{H}_2\text{O}] \times J(O^1D) \quad (\text{R2})$$

Figure 5 shows scatter plots of HCHO vs. ($\text{O}_3 \times \text{H}_2\text{O}$) from model results and from measurements with Hantzsch and LP-DOAS. Only data from afternoon hours (11:00–17:00 LT) on fair weather days were used. The slopes of the regressions in Fig. 5 are 1.67, 1.96 and 4.65 for model, Hantzsch and LP-DOAS, respectively. As expected, the model agrees better with the in-situ Hantzsch than with the remote sensing LP-DOAS. This indicates that model and in-situ data represent air masses with similar VOC chemistry. Results from the remote sensing instrument (LP-DOAS), show that the instrument sampled different air masses with very high HCHO levels. The LP-DOAS measurements are influenced by local biogenic emissions, which are not seen as average conditions in the model's grid cell. Because the model does not contain primary HCHO emissions, this comparison is based on the assumption that all HCHO at this site are secondary produced. This is reasonable since there are no significant direct emissions of HCHO around Alzate, and also the lifetime of HCHO is short compared to the advection time. The agreement between the model and the Hantzsch measurements shows that the model is able to reproduce the formaldehyde mixing ratios in a satisfactory way. It is important to keep in mind, when comparing model results and measurements, that the instrument setup and type have to be taken into account.

4.2 Concentrations and temporal variations at Bresso and Alzate

Figure 4 shows the temporal variation of model results close to the surface and measured concentrations of O_3 , HCHO, CO and NO_2 at Bresso (left panel) and Alzate (right panel) with 3 h resolution between 22 July and 20 August.

During the campaign period, the highest daily surface ozone maximum was around 90 ppbv. Compared with the measurements from PIPAPO in May–June 1998 (the highest level was 190 ppbv) and the levels in September–October 2003 FORMAT campaign

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(the highest level was 135 ppbv) at the same location, the concentration is unexpectedly low for this time of the year. These relatively low maximum levels can be explained by unstable weather conditions in this period, or by the low emissions during the Italian summer vacation in August. According to the emissions inventory from CITY DELTA, both CO and VOC emissions decrease by about 15% because of the lower industrial activity during the summer vacation. NO_x emissions is only 5% lower, because the reduced work related traffic was compensated by increased tourist traffic during this period.

Afternoon O₃ levels are usually correlated with temperature in summer (e.g. Neftel et al., 2002; Weber and Prévôt, 2002; Ordóñez et al., 2005). Figure 6 shows the regression of the afternoon ozone mixing ratios against temperature for three campaigns: PIPAPO 1998, FORMAT 2002, and FORMAT 2003. The slope of the linear regression between O₃ concentration and temperature was rather small for the FORMAT 2002 campaign in comparison to the PIPAPO and FORMAT 2003 campaign. Both the temperature itself and the other meteorological factors represented by temperature, such as radiation, cloud cover and humidity, affect the photochemical processes (e.g. decomposition of PAN, emission rate of biogenic VOCs, photolysis rates, etc.). The low slope of the ozone vs. temperature regression found in the 2002 campaign shows the influence of unstable weather conditions, and also the effect of the summer vacation on O₃.

Both at Alzate and Bresso, measured and modelled ozone show a typical pattern for the summer time, with low mixing ratios in the night and peaks during the late afternoon. The left panel of Fig. 4 depicts the time series for Bresso, the site most influenced by local emissions. Observed ozone levels during the campaign period for Bresso ranged from a few ppbv up to 95 ppbv. The low ozone levels during nighttime are mainly caused by titration with NO, due to local emissions from the city. Modelled ozone at Bresso is in good agreement with observations both in the magnitude of the O₃ concentrations and the diurnal variation. Measured HCHO, CO and NO₂ show strong influence from local emissions, and some peaks can be ascribed to local sources. There were a few days

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within the last fair weather period when the modeled ozone was lower than measured during the nighttime, and the modeled NO_2 was higher than the measurements. This can be explained by a too low mixing height in the model, trapping emissions during the night and causing significant ozone loss from dry deposition and ozone loss by reaction with NO . At Alzate (right panel), ozone levels and time variation simulated by the model generally agree well with measurements. The model reproduces the ozone concentrations during the daytime, and underestimates the ozone levels during the nighttime, especially during nights with clear sky. In the same way as in Bresso, this might be due to an overestimated influence of dry deposition close to the surface during the nighttime. Since 18 August was a Sunday, the drop of O_3 , CO and NO_2 possibly due to the weekend effect. On 11 August, which was the day with precipitation, the model calculated much higher levels for ozone and HCHO than the observations. That day the NWP model didn't produce any rainfall, and the temperatures were overestimated as well. This explains the discrepancy.

Both CO and NO_x have a large number of emission sources in the Po Basin. The median CO concentration at Bresso is only about 285 ppbv, following the reduced emissions during this period. The results from Bresso indicate that the model is able to provide good estimates of both CO and NO_2 mixing ratios. The simulated concentrations of CO and NO_2 are generally underestimated at Alzate, mainly due to the averaged emissions in the model grid cells. The results from Alzate show that the thermally induced circulation was more clearly identified by the model, that clean air arrived from the mountains in the night, and that polluted air arrived from the south in the early or late afternoon. The modelled evening peaks of CO and NO_2 at Alzate suggested that the model was able to capture the afternoon arrival of the plume from the south, but the modelled transport from the north in the morning was too strong.

North Foehn events were identified on 7, 12 and 13 August, where strong winds from the Alpine crest brought dry and clean air from the free troposphere. On 13 August, the meteorological data showed weaker Foehn character than on the other two days. Despite high temperature and radiation, the observed ozone levels remained

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below 60 ppbv both at Alzate and Bresso during these days. Such mixing ratios are representative of high altitude air above the Alps (Weber and Prévôt, 2002). Also the CO and NO₂ observations showed low mixing ratios: CO was about 200 ppbv at Bresso and 100 ppbv at Alzate. The model is in good agreement with measurements during the identified North Foehn days.

4.3 Slopes of O₃ versus NO₂ at Alzate

During the campaign, the last identified fair weather period, i.e. IOP (13–20 August) had the most stable weather conditions. For several days, the ground O₃ levels measured at Alzate were around 90 ppbv, and the highest O₃ level (127 ppbv) was measured in an area southwest of Alzate at 14:00 h on 17 August by the aircraft. Except the North Foehn day (13 August), the weather conditions were similar for all these days. Overall the northerly winds from the Alps during the night and change to southerly about 08:00–09:00 LT in the morning, and then the southerly winds last until 20:00 LT. During the campaign the south-southeast winds are dominating during the daytime, and the wind speeds are ~1.5 m/s. This means that air masses from the edge of Milan metropolitan area need 3–4 h to reach Alzate. For ozone production sensitivity studies, ozone production efficiency is important. In some cases, the slope of O₃ versus NO₂ ($\Delta\text{O}_3/\Delta\text{NO}_2$) can be interpreted as the ozone production efficiency, i.e. as the number of O₃ molecules produced for each NO_x consumed, where NO₂ (NO_y-NO_x) represents consumption of NO_x (Lin et al., 1988, Trainer et al., 1993). Thielmann et al. (2002) studied several cases at Alzate by analyzing the measurements, and concluded that the ozone production in the Milan plume is strongly controlled by VOCs. They found that $\Delta\text{O}_3/\Delta\text{NO}_2$ was about 2.2, and the ozone background level was 93.1 ppbv during the afternoon hours (15:00–17:00 LT) in May 1998. Prévôt et al. (1997) performed aircraft measurements over the Southern Alps in July 1993. A $\Delta\text{O}_3/\Delta\text{NO}_2$ value of 4.2 was found for the flight route in the vicinity of Alzate, whereas $\Delta\text{O}_3/\Delta\text{NO}_2$ was 13.6 for the more rural areas.

Figure 7 illustrates both modeled and measured scatter plots of O₃ vs. NO₂ at Alzate.

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In the figure, both measurements and model results are averaged between 12:00 h and 17:00 h. The slope of O_3 vs. NO_z is 4.9 for the measurements and 5.1 for the model. This value is higher than the value 2.2 calculated by Thielmann et al. (2002), who found that Alzate was strongly influenced by the Milan plume. Our results are very similar to the value presented by Prévôt et al. (1997), where the aircraft flew over a large area influenced by the regional plume. The differences can be explained by the location of the plume and strength of the plume due to the less emissions by vacation effect. Since the dominating winds come from the southeast, Alzate might be located on the edge of the plume, and hence not so strongly influenced by the urban plume. This is supported by the measurements of NO_z and nitrates (not shown) at Alzate, that both peaked at the same time as O_3 , although the levels were low. The decreased emissions due to the vacation effect can be another reason for lower O_3 production in this period, since the ozone production obviously depend on the levels of precursors (Liu et al., 1987, Lin et al., 1988).

Similar O_3 background levels during the afternoon hours have been calculated from both data sets: 33 ppbv for model and 35 ppbv for measurements (see the intercepts in Fig. 7). These levels are much lower than those in Thielmann et al. (2002) and Prévôt et al. (1997). They reported 93.1 ppbv for the afternoon hours in May 1998 at Alzate, and 79.4 ppbv for the areas in the vicinity of Alzate in July 1993, respectively. The background levels of O_3 during the afternoon hours represent the levels in the well-mixed boundary layer. They give information on emissions and the ozone build up based on the meteorological conditions. During the last fair weather period, the combined photochemical production and background levels produced O_3 peak levels of about 90 ppbv at Alzate. The low background levels due to lower emissions and unstable weather conditions play an important role for the magnitude of the O_3 peaks.

4.4 Comparison with aircraft measurements

The period from 13 to 20 August was characterized by stagnant conditions, which is favourable for ozone production and accumulation. A total of 6 flights (13, 14, 15, 16,

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17 and 18 August) were performed during this period. Figure 8 shows modelled and measured O_3 and HCHO along the flight tracks on 15, 16, 17 and 18 August. Data measured on 13 and 14 August were excluded, because of calibration problems on 13 August and because of shortage of data on the 14 August.

Because of the thermal winds from the south during day time, both HCHO and O_3 were expected to peak in areas to the north of Milan. On 15, 16 and 17 August, the ozone peaks were measured by aircraft at about 15:00 LT, in areas north of Milan. The peak values were 104 ppbv on 15, 123 ppbv on 16, and 127 ppbv on 17 August. The meteorological conditions were similar for these three days. Since the flight on 15 August mainly took place over areas north, east and south of Milan, the flight track did not cross the Milan plume. However, the fact that both aircraft measured ozone and formaldehyde mixing ratios (104 and 5.22 ppbv of maximum concentration, respectively) as well as the aerosol concentrations (not shown) were elevated and peaking at the same location shows that the measured air mass was influenced by the pollution from the urban area of Milan. The flight on 18 August started earlier, finished at about 13:00 h and covered the area of the north and east of Milan. Southeast winds were dominating during this flight, and the highest ozone level measured was 82 ppbv north of Milan at around 12:00 LT, too early to catch the Milan plume. The model results along the flight tracks show good agreement with the measurements. The comparison of mixing ratio levels and their temporal variation indicates that the model is able to reproduce the O_3 and HCHO most of the time both for transport and photochemical processes in this area. Some HCHO peaks are not captured. These peaks are possibly caused by local primary emissions. Analyses of FORMAT data suggest that the HCHO in the northern part of the Po Basin is mainly photo-chemically produced (manuscript in preparation), but more observations and modelling will be needed to distinguish between primary and secondary HCHO in this area.

Figure 9 shows the flight track followed by the aircraft on 17 August. The colour coding represents the mixing ratios of ozone (left hand panel) and HCHO (right hand panel). From this figure one can clearly see that the Milan plume was located north-

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west of the city. Both O_3 and HCHO measurements distinguish the plume from the surroundings. Measured O_3 levels were above 120 ppbv inside the plume, and surrounding areas have ozone levels around 90 ppbv. After a few days of build-up due to fair weather, both surface and aircraft measurements indicate the highest ozone levels on this day. The model ozone levels above 120 ppbv were found up to 700 m in a well-mixed boundary layer, which agrees well with the aircraft measurements made at about 300 m. The simulated HCHO peak was above 7 ppbv close to the surface, and about 6 ppbv at the flight altitude. This is in fairly good agreement with the measured value of 5 ppbv by aircraft, and the ground level of 3–6 ppbv measured by LP-DOAS at Alzate.

The modelled spatial distributions and levels of O_3 , HCHO , NO_y and CO in the Po Basin close to the surface at 14:00 h on 17 August are shown in Fig. 10. The 2 ppbv HCHO contour (lower left panel) is covering a large area. This is caused by a combination of secondary formaldehyde produced by the oxidation of both anthropogenic and biogenic VOC emissions. The upper and lower right panels of Fig. 10 show the distribution of NO_y and CO , respectively. Close to the surface, the spatial distribution of total reactive nitrogen NO_y reflects the combined influence of the emissions and transport. NO_y levels were about 15–20 ppbv downwind of Milan. Inside and in the immediate vicinity of Milan (including Bresso) the NO_y mixing ratio was above 20 ppbv. CO can be used as a tracer of emissions because of its long lifetime. CO levels up to 400 ppbv were found in the city of Milan, and about 300 ppbv of CO was observed inside the urban plume. This is low compared to the 850 ppbv measured inside the plume on a day in May 1998 (Thielmann et al., 2002). The measured plume was located east of 9°E (Fig. 9), and the modelled plume was further to the west (Fig. 10). Since there was no aircraft data available west of 9°E , it is difficult to assess the real width of the plume in this case. The difference between the modelled and measured locations of the urban plumes seems to be due to the differences between the modelled and real wind directions. The modelled winds were from southeast, and the data was updated every 3 h. The measured winds were mainly from the southeast as well, but were sometimes

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from the south. The underestimated O_3 and HCHO levels on 17 August shown in Fig. 8 can therefore be explained by the fact that the flight track is to the east of the modelled plume but partly inside the real plume. Dommen et al. (2002) suggested that downwind of the Milan metropolitan area, a regional plume was 50 km wide and atop of this the urban plume was 10–15 km wide. They also concluded that the background ozone levels in the Po Basin for those days were around 80–130 ppbv, ozone levels were 15–30 ppbv higher in the regional plume, and the urban plume added another 10–30 ppbv. Therefore, the difference in O_3 mixing ratios between the urban plume and the surroundings was about 45–60 ppbv in 50 km distance. Our model produces an urban plume of about 15–20 km width, with O_3 mixing ratios about 40–50 ppbv higher than outside the regional plume. The measured urban plume on 17 August in 2002 is about 10 km wide, and the levels are similar to our model results. The ozone gradients in the area north of Milan result from both anthropogenic and biogenic emissions. The comparison shows that the model is able to reproduce reasonably the O_3 mixing ratios in background air and in the photochemically produced urban plume reasonably well.

5 Conclusions

The NILU RCTM model has been applied to reproduce the photochemical evolution over the Milan metropolitan area during the FORMAT summer campaign of 2002, which took place between 22 July and 20 August. The model results were evaluated with measurements from two surface sites and aircraft data. The comparison shows that the time variation agrees well with the measurements both at urban and semi-rural sites. The discrepancies for CO and NO_2 are mainly caused by local sources at Bresso, which are not identified in the model. The underestimated CO and NO_2 levels at Alzate possibly are due to model resolution. The ozone peaks values are well reproduced by the model. Both model results and measurements show low background O_3 levels of about 35 ppbv during the 2002 campaign. The reasons for the low O_3 levels can be ascribed to the low emissions in August and unstable weather conditions. The slopes

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of O₃ versus NO_z of 5.1 and 4.9 are calculated from model results and measurements at Alzate, respectively. This indicates that the model has a reasonable representation of the ozone chemistry.

As the main target of the FORMAT project, HCHO was intensively measured during the campaign period with various techniques. The modelled HCHO has been evaluated with data from different instruments. At the semi-rural site Alzate, the model results were compared with data from both an in-situ instrument (Hantzsch) and a remote sensor (LP-DOAS). The measured HCHO from these two instruments shows large differences during fair weather days. The HCHO measured by LP-DOAS are sometimes twice the levels measured by the Hantzsch instrument. Local natural VOC emissions can explain the differences, because the light path of the LP-DOAS passed over a forest with strong isoprene emissions leading to fast HCHO formation, in particular on sunny days. In this case, the model results are close to the in-situ measurements, since both of them represent the general conditions of this location (forests are sparse in the Po basin). The scatter plot of HCHO versus (O₃ × water vapour) also indicates that the model and the in-situ instrument are representing similar air masses and photochemistry, while the LP-DOAS is measuring a different air mass with higher VOC concentrations. This comparison demonstrates the importance of the experimental configuration since different instrumental setups can, depending on the surroundings, lead to highly different measurements. In-situ and remote sensing equipment, even when they are set up at the same location, are very often sampling air parcels with different contents of HCHO.

The comparison with aircraft data shows that both the aircraft and model captured the plume on 17 August. Because of multi-days ozone build up, this was the day that both the model and the measurements show the highest ozone peak above 120 ppbv downwind of the Milan area. The measured plume was both observed and simulated northwest of Milan between 13:00 h to 14:00 h local time, about 30 km away from the city. The model results agree well with measurements on the concentrations. The location of the plume was at the same latitude but slightly shifted to the west. This shift

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is caused by the wind data used in the model, since the wind blows from the southeast in the model, whereas it was blowing from the south-southeast in reality. There are some aspects in which the model simulation might be improved in the future. Model runs with higher horizontal resolution are needed. HCHO should be added as a primary emission source in the emission inventory. Higher resolution and more detailed land use data are needed for more specific information on biogenic emissions in this area. This is especially important for isoprene emissions, which depend on the forest type and solar radiation.

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Table 1. Ground based measurement techniques and measured parameters during the 2002 FORMAT campaign.

Instrument type	Sampling	Sites	Components
DOAS Long Path	Long Path	Alzate	HCHO, O ₃ , NO ₂ , HONO, SO ₂
EnviroNics 300 UV absorption	In-situ	Alzate	O ₃
Hantzsch	In-situ	Bresso and Alzate	HCHO
DOAS White-cell	In-situ	Bresso	HCHO, O ₃ , NO ₂ , HONO, SO ₂
FTIR White-cell	In-situ	Bresso	CO, HCHO
DNPH	In-situ	Bresso and Alzate	HCHO
CO analyser AL5002	In-situ	Alzate	CO
(Vacuum ultraviolet fluorescence)			
Thermoenvironment 42c	In-situ	Alzate	NO
(Ozone chemiluminescence)			
NO _x TO _y instrument (luminol chemiluminescence + NO _y converter)	In-situ	Alzate	NO ₂ , NO _z , NO _y , PANs, total nitrate
Meteo. station		Bresso/Alzate	T, P, relative humidity, wind direction and speed, global radiation

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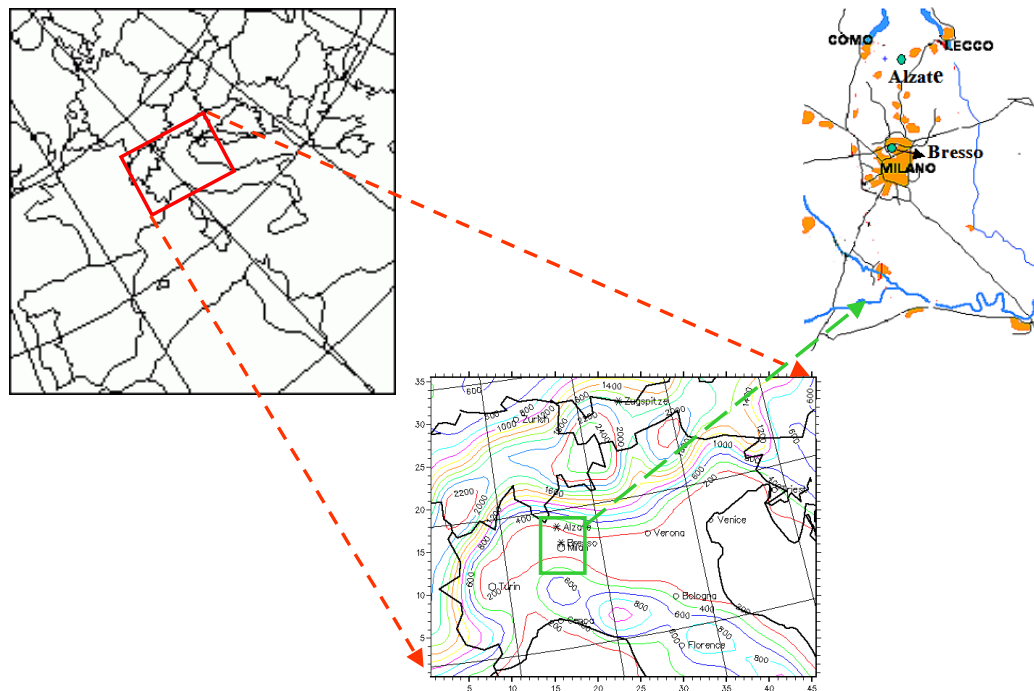


Fig. 1. The model domains for 50 km and 15 km resolutions, and campaign area in Po Valley. The position of the 15 km fine domain nested in the 50 km domain is outlined with a red rectangle. Ground based sites were located in the north of Milan, Bresso (urban site) and Alzate (semi-rural site).

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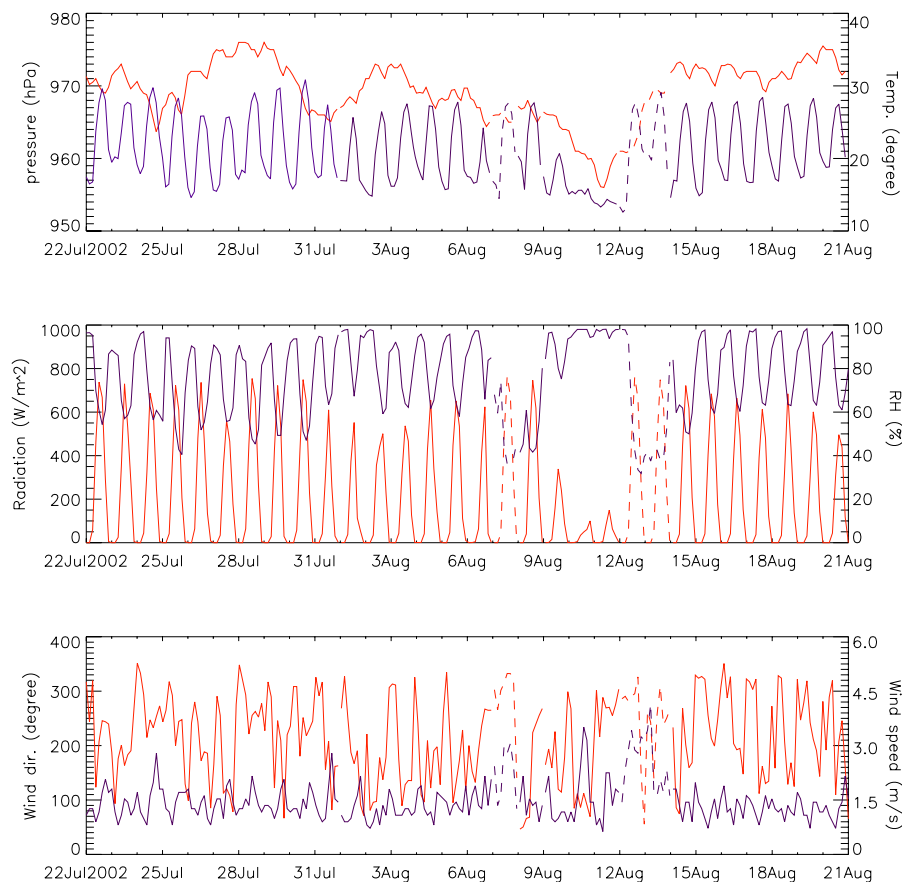


Fig. 2. Meteorological conditions measured at Alzate during the campaign period. The north Föhn days are marked by dashed lines, the episodes are characterized with high wind speed and low relative humidity. 1st panel: pressure (red) and temperature (blue); 2nd panel: global radiation (red) and relative humidity (blue); 3rd panel: wind direction (red) and wind speed (blue).

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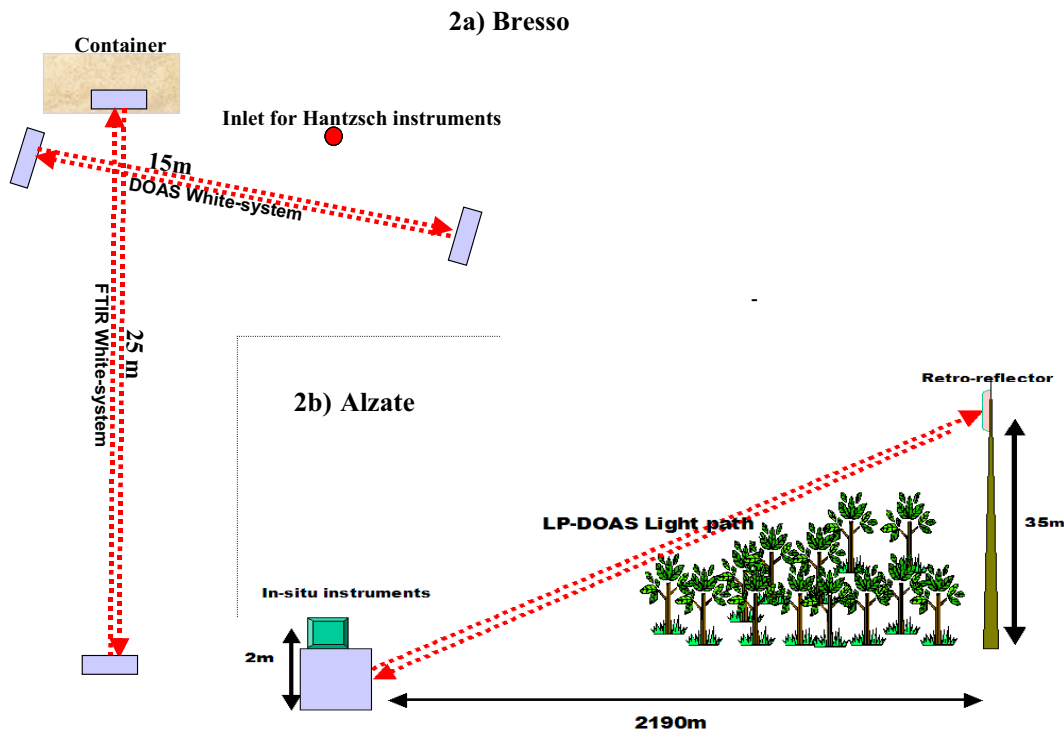


Fig. 3. Instruments set up at two surface stations. **(a)** Ground based instruments set up at Bresso (in-situ instruments only); **(b)** Instruments set up at Alzate (both in-situ and remote sensing instruments).

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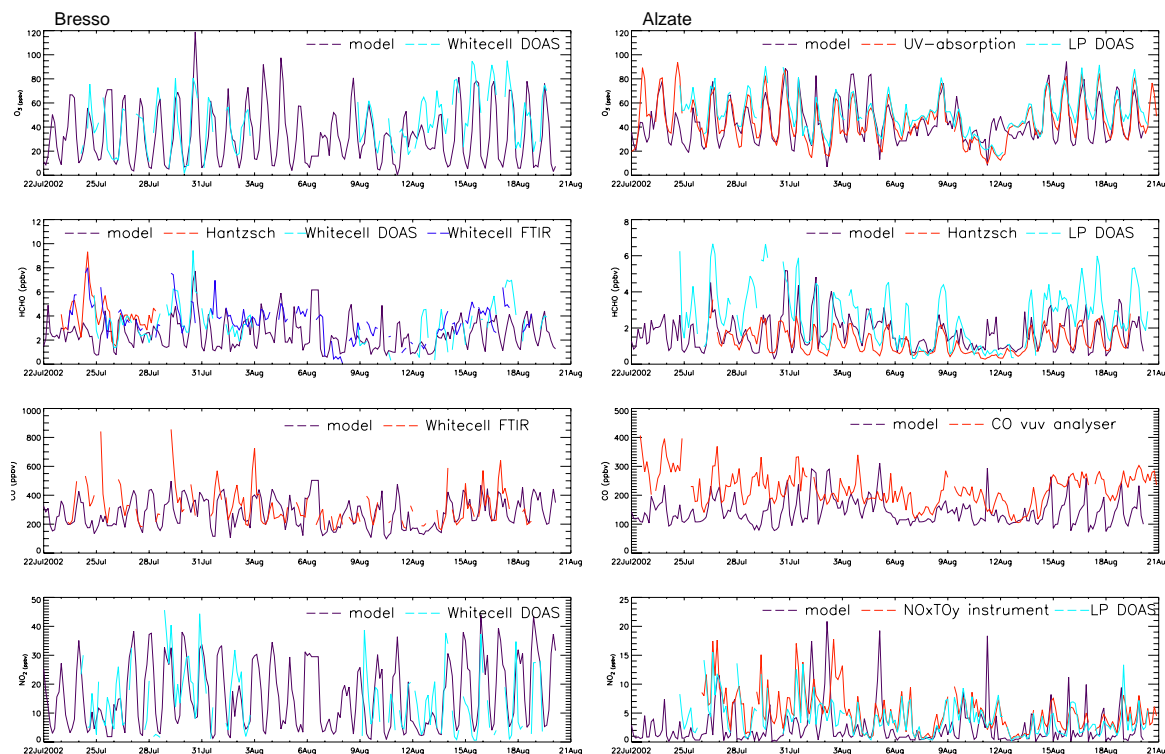


Fig. 4. Modeled and measured mixing ratios of O_3 , HCHO, CO, NO_2 every 3 h (LT) at Bresso and Alzate during the campaign period.

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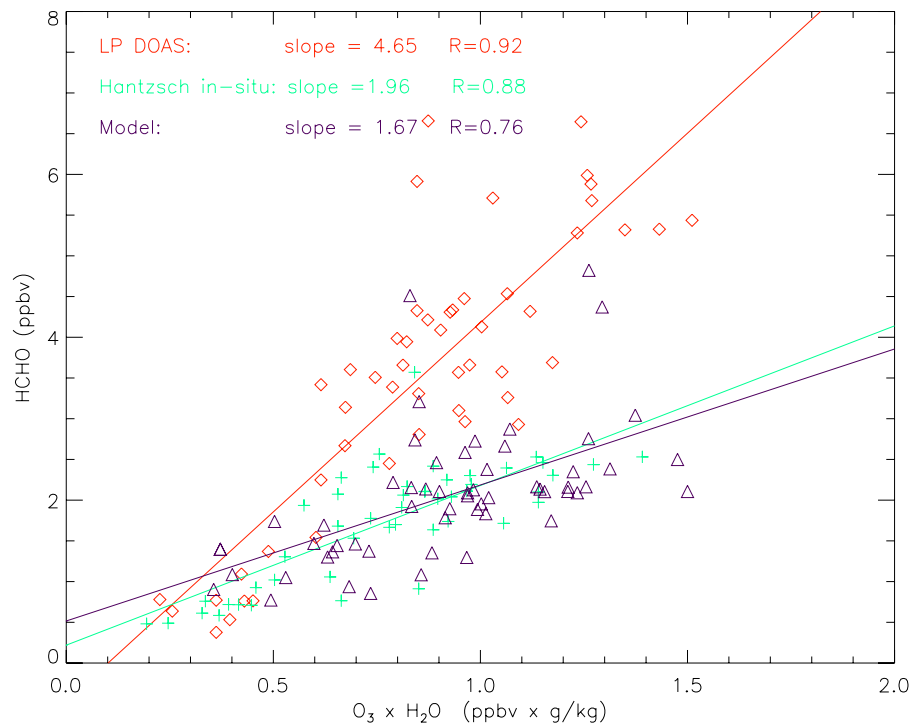


Fig. 5. Scatter plot of HCHO vs. ($O_3 \times$ specific humidity) for model results and measurements from both in-situ and remote sensing instruments at Alzate. Only afternoon data from fair weather days are used. O_3 and HCHO are in ppbv, and water content is g/kg.

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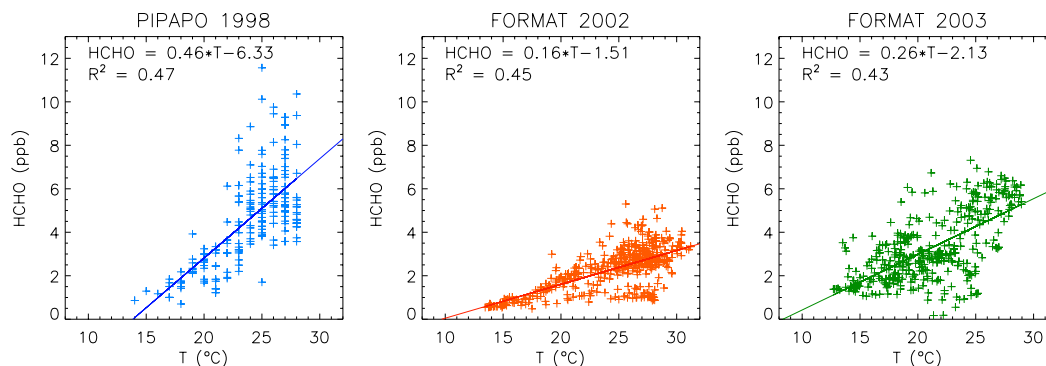


Fig. 6. Regression of the afternoon ozone concentrations against temperature for three field campaigns: PIPAPO 1998 (May–June), FORMAT 2002 (July–August), and FORMAT 2003 (September–October).

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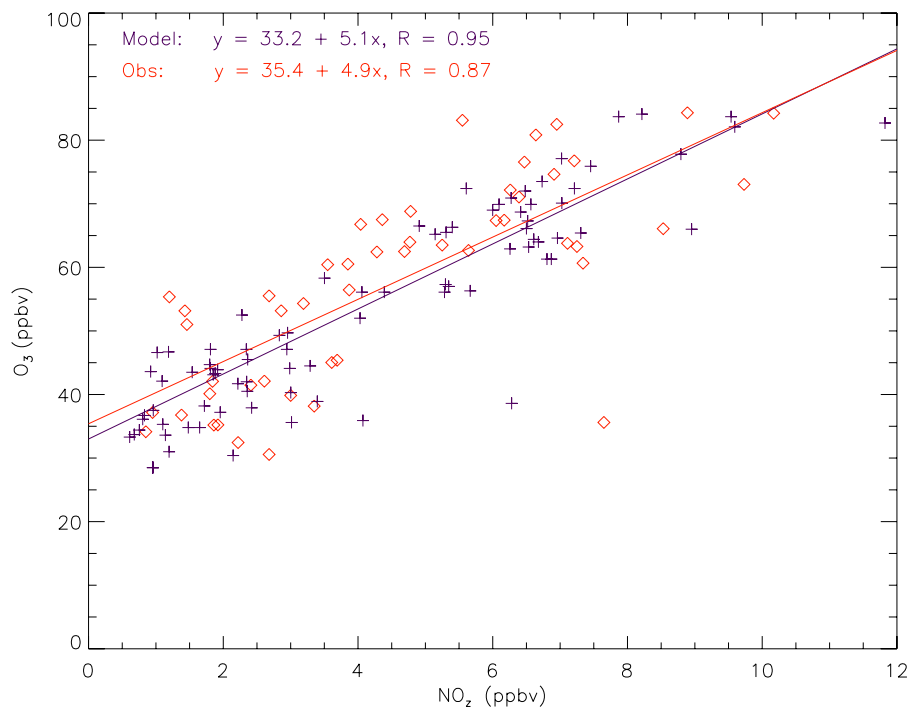


Fig. 7. Scatter plot of both modeled and measured O_3 and NO_2 at Alzate during the fair weather period. Both measurements (UV absorption) and model results were 3-h resolution.

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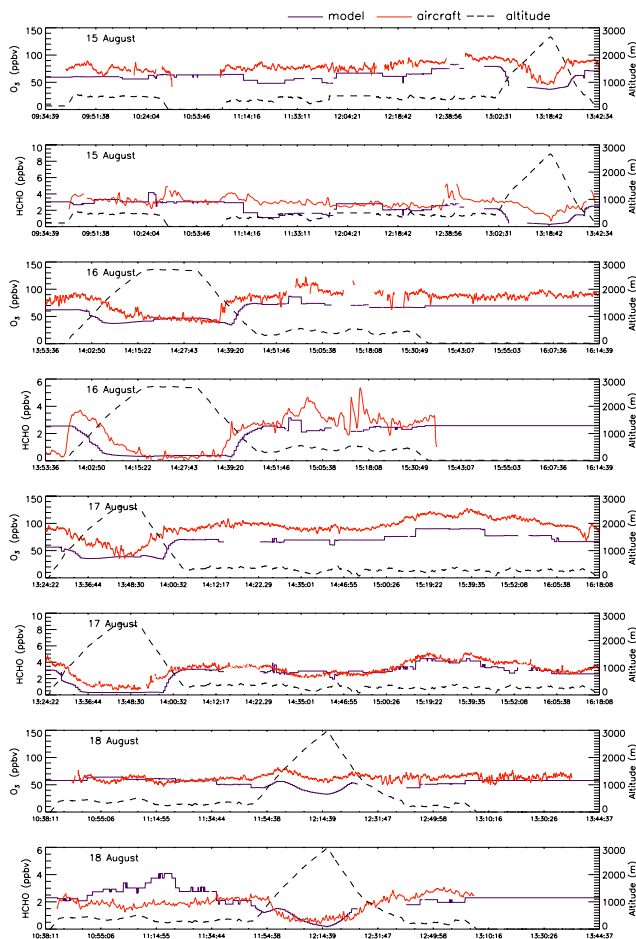


Fig. 8. Simulated (violet) and measured (red) HCHO and O₃ concentrations along the flight tracks (Local Time). The flight height is given by the dashed line.

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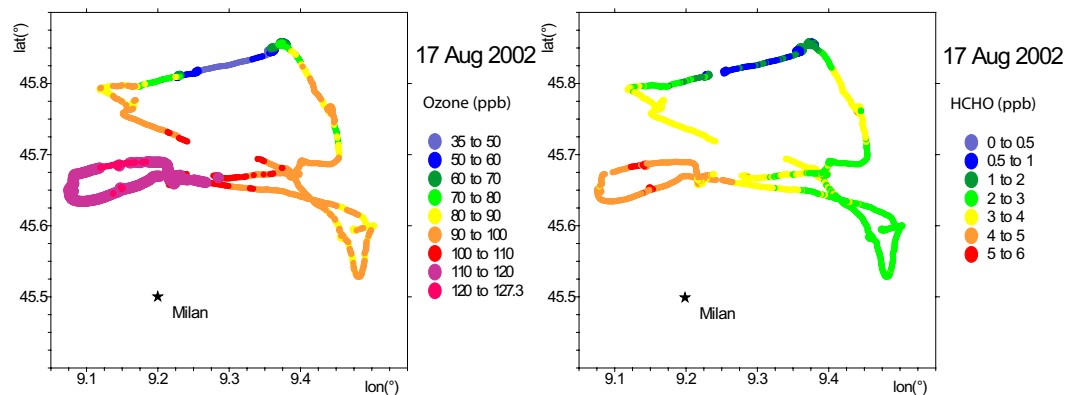


Fig. 9. HCHO and O₃ concentration measured during the flight on 17 August 2002.

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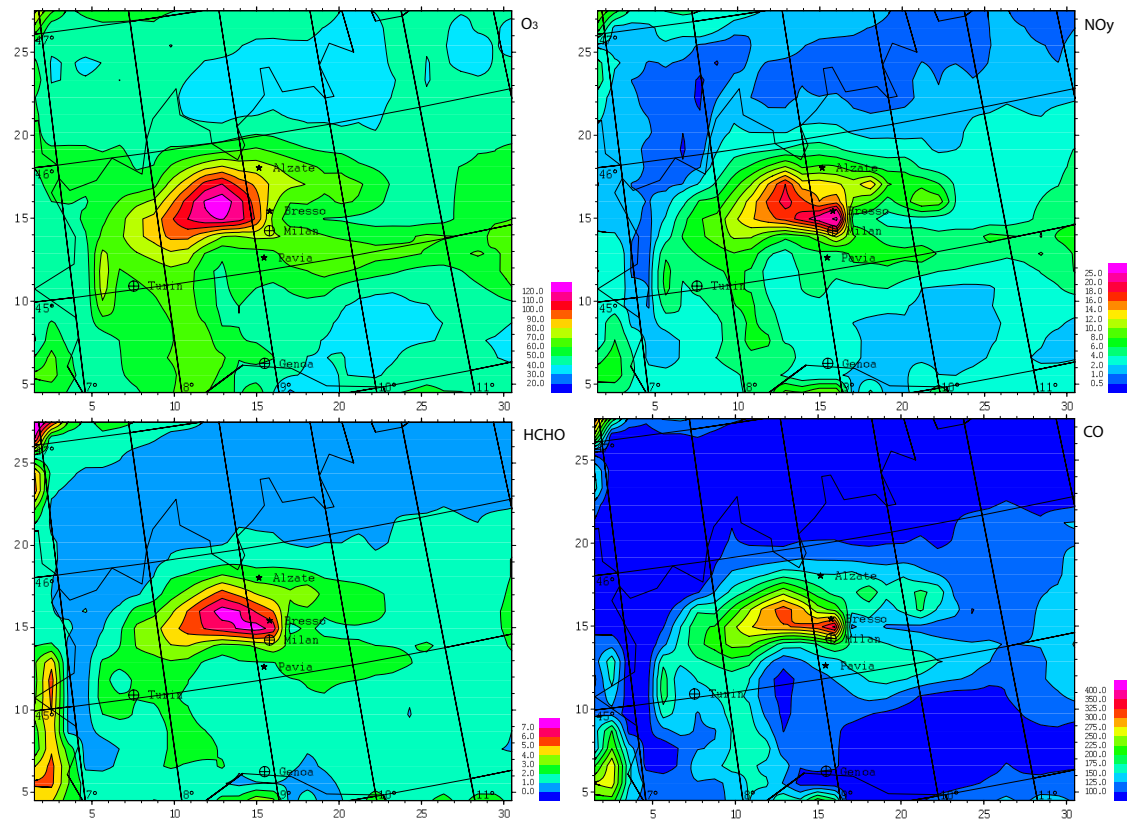


Fig. 10. Spatial distribution of O₃, HCHO, NO_y and CO in the Po Valley, at 14:00 on 17 August. The aircraft captured the highest ozone level above 120 ppb in areas northwest of Milan city. The model results show good agreement with aircraft data.

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